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Long-Lived Porphyrin Cation Radicals Protected in Unimer Micelles of Hydrophobically-Modified Polyelectrolytes

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ABSTRACT: Amphiphilic terpolymers [consisting of ca. 40 mol % sodium sulfonate group, ca. 60 mol % lauryl (La) or cyclododecyl (Cd) group, and 0.1−0.2 mol % zinc(II) tetraphenylporphyrin (ZnTPP) moiety] form unimer micelles in aqueous solution, and the ZnTPP moieties are compartmentalized in the hydrophobic microdomains in the unimer micelles, leading to an extraordinarily long-lived triplet excited state of the ZnTPP (^{3}ZnTPP*). Electron transfer from the long-lived ^{3}ZnTPP* to phenylmethylphenacylsulfonium *p*-toluenesulfonate (PMPS), a self-destructive electron acceptor, which is electrostatically concentrated on the surface of the unimer micelle, generates porphyrin cation radicals (ZnTPP$^{\bullet+}$) within the hydrophobic microdomain. Since the ZnTPP chromophores are protected from the bulk aqueous phase, subsequent reaction between the resulting ZnTPP$^{\bullet+}$ and phenacyl radical from PMPS is prevented. Thus, the porphyrin cation radicals are efficiently accumulated under steady-state irradiation of visible light. The unimer micelle consisting of Cd groups provides a much better protection for ZnTPP$^{\bullet+}$ than that consisting of La groups; a significant amount of the porphyrin cation radical persisted for more than 1 day in the unimer micelle consisting of the Cd groups.

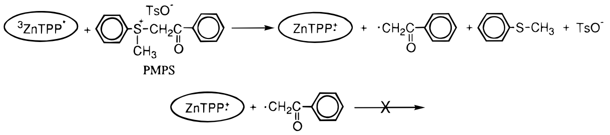
Introduction

Copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and methacrylamides *N*-substituted with bulky hydrophobic groups, such as lauryl (La), cyclododecyl (Cd), adamantyl (Ad), and naphthyl (Np) groups, form "unimer micelles" in aqueous solution due to entirely intramolecular self-association of the side-chain hydrophobes.[1−4] In a previous paper, we proposed a pictorial model for such unimer micelles based on characterization studies by light scattering, SAXS, fluorescence, NMR relaxation, and IR techniques.[4] In the case of the La group, the unimer micelle is formed only when the concentration of the copolymer is lower than ca. 0.5 wt %, whereas the copolymers bearing the hydrophobes with cyclic structures form unimer micelles independent of the polymer concentration.[4] In these unimer micelles, the side-chain hydrophobes are so tightly packed in hydrophobic microdomains, especially in the case of the cyclic hydrophobes, that their local motions are highly restricted.[3,4]

The hydrophobic microdomains consisting of the bulky cyclic hydrophobes in the unimer micelles provide highly constraining microenvironments for chromophores, such as pyrene,[5] azobenzene,[6,7] and zinc(II) tetraphenylporphyrin (ZnTPP),[8−11] if they are covalently incorporated into the copolymers. In these constraining microenvironments, their photophysical and photochemical properties are greatly modified.

We previously reported the spectroscopic behavior of ZnTPP moieties encapsulated in the unimer micelle, which includes absorption, fluorescence, phosphorescence, and excitation spectra.[8,10,11] When the ZnTPP moieties are compartmentalized within the hydrophobic microdomains formed from the clusters of Cd groups in a unimer micelle, the triplet excited state of the ZnTPP (^{3}ZnTPP*) moieties became extraordinarily long-lived because triplet−triplet (T−T) annihilation and quenching by impurities were completely prevented.[8,11] The ZnTPP species are buried in the hydrophobic microdomains, and they are isolated and protected from the aqueous phase. Due to the long-lived triplet state, the ZnTPP moieties in the unimer micelle emit phosphorescence and E-type delayed fluorescence in aqueous solution at ordinary or higher temperatures.[10,11]

Scheme 1. Electron Transfer from Triplet Excited ZnTPP in the Unimer Micelle to PMPS



The present paper is concerned with electron transfer (ET) from the long-lived ^{3}ZnTPP* compartmentalized within the unimer micelle to a self-destructive electron acceptor present outside of the unimer micelle in aqueous solution. We employed an onium salt, phenylmethylphenacylsulfonium *p*-toluenesulfonate (PMPS), as the self-destructive electron acceptor. Being a cation, PMPS should be localized on the anionic surface of the unimer micelle. Photoinduced ET to onium salts and their subsequent decomposition have been well documented.[12,13] The redox potential of phenylmethylsulfonium cations is strongly dependent on their leaving groups.[14] Thus, one can change the reduction potential in a wide range by changing the leaving group. Since the half-peak reduction potential of PMPS is −0.60 V vs SCE, the energy gap for ET from ^{3}ZnTPP* to PMPS is estimated to be −0.04 V. Upon ET from ^{3}ZnTPP*, PMPS decomposes at a fast rate (within ca. 200 ps[12,13]) into phenyl methyl sulfide and a phenacyl radical, leaving a ZnTPP cation radical (ZnTPP$^{\bullet+}$) behind (Scheme 1). The reaction between the resulting ZnTPP$^{\bullet+}$ and the phenacyl radical, which usually follows the photoinduced forward ET in homogeneous solutions, is prevented in the unimer micellar system because the ZnTPP$^{\bullet+}$ and phenacyl radical species are separated inside and outside the unimer micelle, respectively. Thus, the porphyrin cation radicals tend to accumulate.

We wish to report an efficient accumulation of ZnTPP$^{\bullet+}$ within the unimer micelle consisting of the Cd groups where ZnTPP$^{\bullet+}$ is strongly protected as com-

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pared with that in the unimer micelle consisting of the La groups where ZnTPP$^{\bullet+}$ is moderately protected.

Experimental Section

Polymers. A terpolymer of 0.1 mol % zinc(II) 5-(4-acrylamidophenyl)-10,15,20-triphenylporphynate (ZnAATPP), 60 mol % *N*-cyclododecylmethacrylamide (CdMAm), and 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) and a terpolymer of 0.2 mol % ZnAATPP, 60 mol % *N*-laurylmethacrylamide (LaMAm), and AMPS were prepared as reported previously.[8] A copolymer of 0.1 mol % ZnAATPP and AMPS was also prepared as previously.[8]

Other Materials. 5,10,15,20-Tetrakis(4-sulfonylphenyl)-porphinatozinc (ZnTSPP) was prepared according to the literature.[15] PMPS was prepared as described in the literature.[14]

Water was doubly distilled and deionized by passing through an ion-exchange column.

Measurements. Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer at room temperature.

Fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer at room temperature with excitation at 532 nm, the same wavelength as in the laser photolysis described below.

Transient T−T absorption spectra were observed by laser photolysis using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at second harmonic (532 nm). The details of the laser photolysis were reported elsewhere.[11]

ESR spectra were measured on a JEOL Model JES-1X ESR spectrometer with a 100 kHz modulation at room temperature. Steady-state visible light ($540 < \lambda < 700$ nm) from a 1 kW high-pressure mercury lamp was used to irradiate the sample solutions with combined filters of Toshiba O-54, IRA-25S, ND-25, and ND-50 placed between the lamp and the sample solution. The concentrations of the ZnTPP residues and PMPS were 100 μM and 10 mM, respectively. The solutions were purged with Ar for 30 min prior to the light irradiation. *G* values were estimated by comparing with the third ($g = 2.033$) and fourth ($g = 1.981$) lines of MnO. Changes in the concentration of the photochemically generated ZnTPP$^{\bullet+}$ with time in the dark were monitored at an ESR peak top at 333.9 mT after irradiation with the visible light for 1 min.

Results and Discussion

The terpolymers [poly(A/Cd/ZnTPP) and poly(A/La/ZnTPP)], reference copolymer [poly(A/ZnTPP)], and water-soluble low molecular weight porphyrin compound (ZnTSPP) employed in the present study are shown in Chart 1. In the terpolymers, the ZnTPP units are compartmentalized within the hydrophobic microdomains in the unimer micelles in aqueous solution and protected from the bulk aqueous phase. This is conceptually illustrated in Figure 1 which is based on a proposed model for unimer micelles.[4] Since the amounts of the ZnTPP units loaded on the terpolymers are very small (0.1−0.2 mol %), each ZnTPP unit is independently encapsulated in the hydrophobic microdomain and is prohibited from encountering others. In the reference copolymer, on the other hand, the ZnTPP moieties are exposed to the aqueous phase.

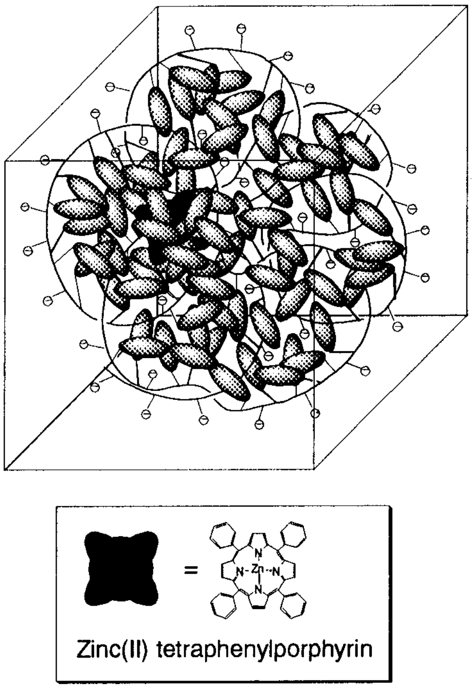
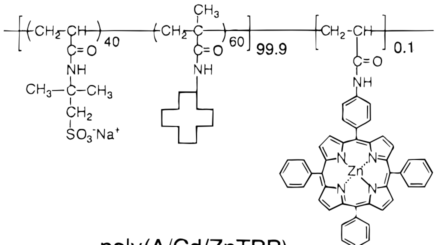
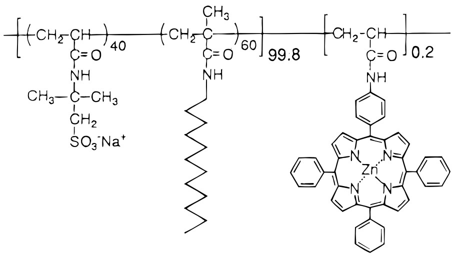


Figure 1. Conceptual illustration of a model for the unimer micelle in which a ZnTPP moiety is compartmentalized.

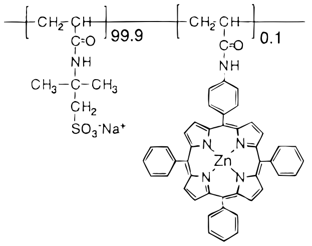
Chart 1



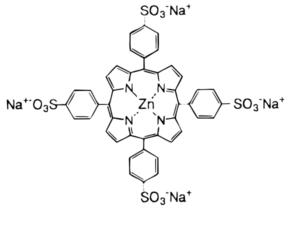
poly(A/Cd/ZnTPP)



poly(A/La/ZnTPP)



poly(A/ZnTPP)



ZnTSPP

ZnTSPP and PMPS form a charge transfer (CT) complex in aqueous solution, and so does the ZnTPP species in the reference copolymer. The Soret absorption bands of ZnTSPP and poly(A/ZnTPP) show red shifts in the presence of PMPS in aqueous solution (Figure 2a,b, respectively) due to the CT complexation. In the case of poly(A/ZnTPP), in which the porphyrin moiety is attached to a fully ionized polysulfonate chain, a significant red shift of the Soret band occurs at a much lower concentration of PMPS (Figure 2b) than in the case of ZnTSPP (Figure 2a) because the PMPS cations are electrostatically concentrated on the polyanion. The CT formation constants (K_{CT}) for ZnTSPP and poly(A/ZnTPP) estimated from these spectral data by use of a Nash's plot[16] are listed in Table 1. The K_{CT} value for poly(A/ZnTPP) is 2 orders of magnitude larger than that for ZnTSPP.

In contrast, the ZnTPP species in poly(A/La/ZnTPP) and poly(A/Cd/ZnTPP) are prevented from contacting PMPS and therefore they show no spectral change due

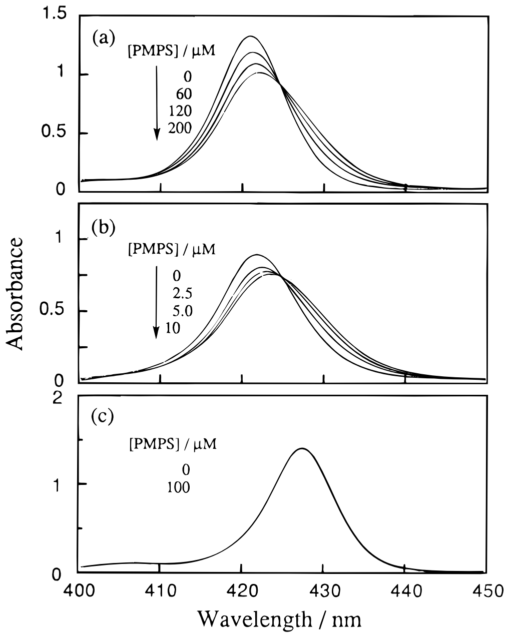


Figure 2. Soret absorption bands for (a) ZnTSPP, (b) poly(A/ZnTPP), and (c) poly(A/La/ZnTPP) in the presence of varying amounts of PMPS in aqueous solution. The residual concentration of the porphyrin moieties is 2 μM.

Table 1. Formation Constant for the CT Complex, Stern−Volmer Constant for Fluorescence Quenching, and Apparent Second-Order Rate Constant for Electron Transfer from Triplet Excited ZnTPP to PMPS in Aqueous Solution

sample	K_{CT}/M^{-1} [a]	K_{SV}/M^{-1} [b]	$k_{q,T}$/M^{-1} s^{-1} [c]
ZnTSPP	3.7×10^3	1.6×10^3	1.7×10^7
poly(A/ZnTPP)	3.2×10^5	7.5×10^4	1.4×10^8
poly(A/La/ZnTPP)	*d*	*e*	3.8×10^6
poly(A/Cd/ZnTPP)	*d*	*e*	1.1×10^6

[a] Formation constant for the CT complex between ZnTPP and PMPS. [b] Stern−Volmer constant for ZnTPP fluorescence quenching by PMPS. [c] Second-order equivalent rate constant for ZnTPP triplet quenching by PMPS. [d] No CT interaction. [e] No fluorescence quenching.

to CT interactions even at much higher concentrations of PMPS. Figure 2c shows, as an example, that the Soret absorption band for poly(A/La/ZnTPP) does not change at all in the presence of 10 mM PMPS. Although PMPS cations are concentrated on the anionic surface of the unimer micelle, PMPS cannot come into contact with ZnTPP to form CT complexes because of the chromophore protection.

Fluorescences of ZnTSPP and poly(A/ZnTPP) are quenched by PMPS, as shown in Figure 3a,b, respectively. Fluorescence from the reference copolymer is quenched more efficiently than that from ZnTSPP. The Stern−Volmer constants (K_{SV}) estimated from the data in Figure 3a,b are listed in Table 1. The K_{SV} value for the reference copolymer is 1 order of magnitude larger than that for ZnTSPP due to the electrostatic concentration of the PMPS cations on the polyanion. In the case of the terpolymers, however, little or no fluorescence quenching occurs even at a high concentration of PMPS (10 mM) (Figure 3c). These observations indicate that ET from the singlet excited state (S_1) of the ZnTPP moiety to PMPS can occur only when the porphyrin moieties are exposed to the aqueous phase and that the singlet ET is prohibited when they are compartmentalized in the unimer micelle.

Time-resolved transient absorption spectra in a millisecond time domain for the terpolymers and the reference copolymer in aqueous solution were previously measured by laser photolysis, and the observed transient spectra were assigned to the triplet−triplet (T−T) absorption of the ZnTPP moieties.[8] The T−T absorption decays were monitored at 480 nm in the presence of varying concentrations of PMPS in aqueous solution. To estimate the apparent second-order rate constant ($k_{q,T}$) for ET from ^{3}ZnTPP* to PMPS, pseudo-first-order decay constants (k_T) estimated from the initial slopes of the first-order decay plots for the T−T absorbances are plotted as a function of the concentration of PMPS (Figure 4). The triplet quenching of poly(A/ZnTPP) is much more efficient than that of ZnTSPP, as compared in Figure 4a. Values of $k_{q,T}$ estimated from the slopes of the linear plots for poly(A/ZnTPP) and ZnTSPP in Figure 4a are listed in Table 1. Although the terpolymers show no S_1 quenching with PMPS, they show T_1 quenching due to ET from ^{3}ZnTPP* to PMPS. This is because the T_1 lifetimes of the ZnTPP moieties compartmentalized in the unimer micelles are so long that a long range ET with a slow rate can take place between the ZnTPP chromophore protected inside the hydrophobic microdomain and PMPS species bound on the surface of the unimer micelle. However, the plot of k_T against the concentration of PMPS shows a downward curvature, indicating that the T_1 quenching becomes less effective as the quenching proceeds (Figure 4b). This is due to the fact that the ZnTPP species are buried inside the hydrophobic microdomains with different extents of protection; some ZnTPP species existing near the surface in the microdomain can undergo triplet ET to PMPS located on the surface of the unimer

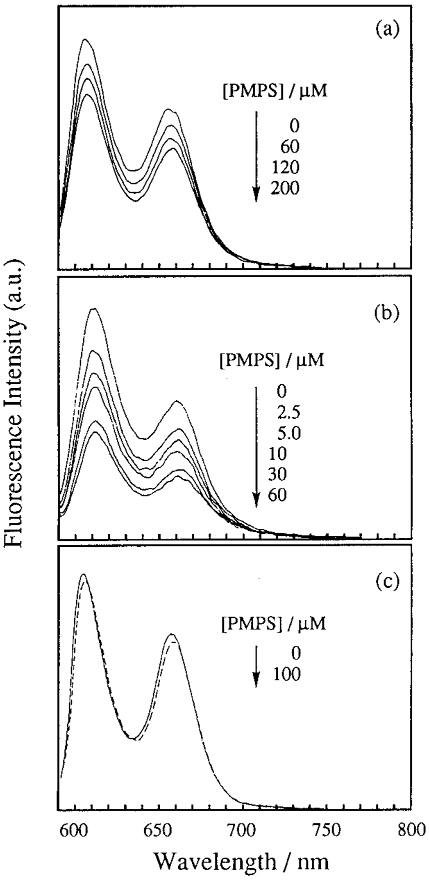


Figure 3. Fluorescence spectra of (a) ZnTSPP, (b) poly(A/ZnTPP), and (c) poly(A/La/ZnTPP) in the presence of varying concentrations of PMPS in aqueous solution. The residual concentration of the porphyrin moieties is 2 μM. The excitation wavelength is 532 nm.

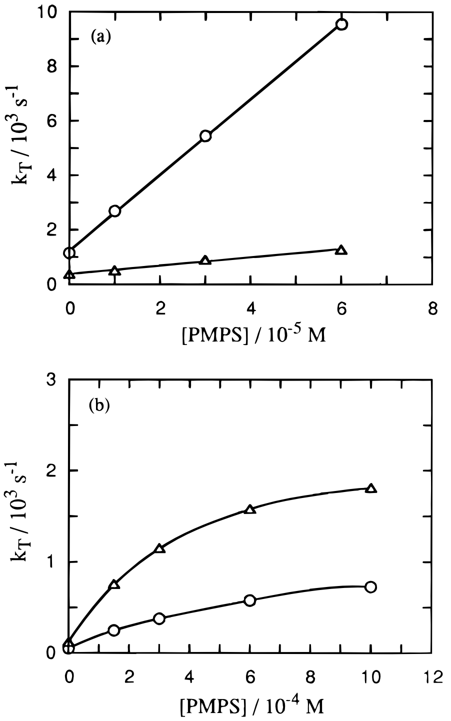


Figure 4. Pseudo-first-order rate constant for the triplet quenching as a function of the concentration of PMPS: (a) (○) poly(A/ZnTPP), (△) ZnTSPP; (b) (△) poly(A/La/ZnTPP), (○) poly(A/Cd/ZnTPP).

micelle, while some ZnTPP species buried deep in the hydrophobic microdomain cannot participate in the ET event. As can be seen from Figure 4b, the extent of the chromophore protection in poly(A/Cd/ZnTPP) is markedly larger than that in poly(A/La/ZnTPP). A similar tendency in the extent of chromophore protection between the Cd and La domains in the terpolymers was observed in the fluorescence quenching of pyrene with Tl^+, pyrene compartmentalized in the corresponding terpolymers.[4] Values of apparent $k_{q,T}$ for the terpolymers estimated from the initial slopes of the plots in Figure 4b are 2 orders of magnitude smaller than that for the reference copolymer (Table 1).

PMPS decomposes rapidly into phenyl methyl sufide and a phenacyl radical upon accepting an electron from $^3\text{ZnTPP}^*$, and thus PMPS acts as an efficient sacrificial electron acceptor (Scheme 1). The reaction between the resulting $\text{ZnTPP}^{\bullet+}$ and the phenacyl radical is prevented in the terpolymer system because the $\text{ZnTPP}^{\bullet+}$ and phenacyl radical species are separated inside and outside the unimer micelle, respectively. Figure 5 shows ESR spectra of aqueous solutions of the terpolymers and reference copolymer containing PMPS measured under steady-state visible light irradiation. It is known that the low molecular weight zinc(II) tetraphenylporphyrin cation radical shows a hyperfine structure (hfs) arising from the eight equivalent *ortho* hydrogens on the phenyl rings in homogeneous solution at room temperature.[17,18] However, the terpolymer systems show ESR spectra with a line width of 4.9 G without hfs (Figure 5). These spectra coincide with that of the low molecular weight $\text{ZnTPP}^{\bullet+}$ in a glassy state at 77 K.[17] This suggests that four phenyl rings in the $\text{ZnTPP}^{\bullet+}$ moieties in the unimer micelles cannot rotate freely because of the rigidity of the hydrophobic microdomain in which the $\text{ZnTPP}^{\bullet+}$ species are compartmentalized. The intensities of the ESR signals for the terpolymer systems are much stronger than that for the reference copolymer system. In the ESR spectrum of the reference copolymer, the hfs due to the delocalization of the radical spin on the phenyl hydrogens[17,18] is not recognizable because the ESR signal is too weak. In the terpolymer systems, the ESR intensity for poly(A/Cd/ZnTPP) is ca. 3.5 times stronger than that for poly(A/La/ZnTPP). These observations indicate that the porphyrin cation radicals significantly accumulate in the terpolymer systems, especially in the poly(A/Cd/ZnTPP) system, under irradiation of steady-state visible light whereas little or no radical accumulation occurs in the reference copolymer system although photoinduced ET to PMPS is much more efficient in the reference copolymer system than in the terpolymer systems.

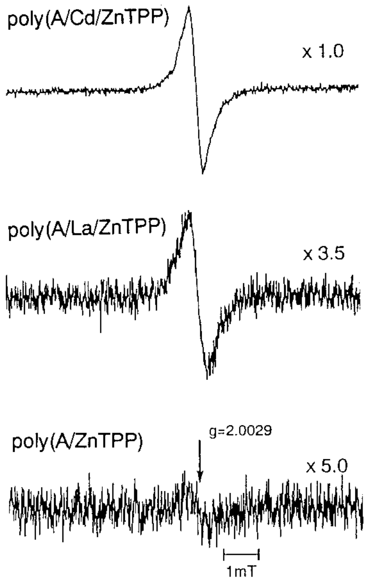


Figure 5. ESR spectra under irradiation of steady-state visible light in the presence of PMPS in aqueous solution at room temperature.

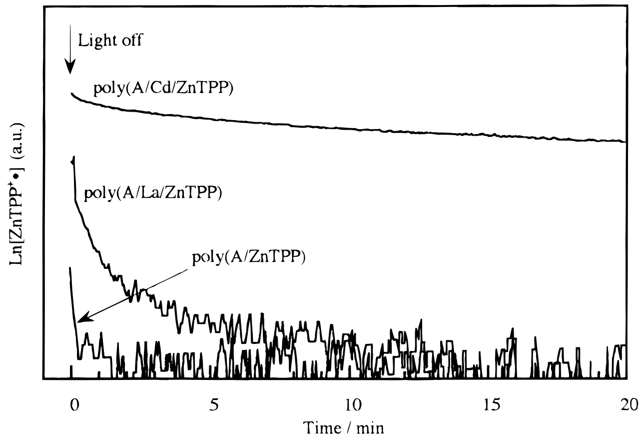


Figure 6. Decay profiles for the ESR absorption at 333.9 mT after irradiation with visible light for 1 min in the presence of PMPS in aqueous solution at room temperature.

ESR signals due to the phenacyl radical were unable to be detected presumably because the lifetime of the phenacyl radical in aqueous solution at room temperature was too short.

Figure 6 compares semilogarithmic plots for the decays of the concentration of $\text{ZnTPP}^{\bullet+}$ in arbitrary units (ESR intensity at 333.9 mT) in the dark after irradiation of visible light for 1 min for the three polymer systems. The initial concentration of the porphyrin cation radical in the poly(A/Cd/ZnTPP) system immediately after the light was turned off was ca. 3 and 16 times higher than those in the poly(A/La/ZnTPP) and poly(A/ZnTPP) systems, respectively. Half-lives are estimated from the decay curves in Figure 6 to be 900, 20, and 6 s for the poly(A/Cd/ZnTPP), poly(A/La/ZnTPP), and poly(A/ZnTPP) systems. In the poly(A/Cd/ZnTPP) system, the decay follows a first-order dependence on time after an initial faster decay in the first 5 min, and a significant amount of ZnTPP$^{•+}$ persists for more than 1 day.

In the terpolymer systems, the decay of the ESR signal is due to rereduction of the porphyrin cation radical because the absorbances of the Soret and Q bands for the ZnTPP chromophores in the terpolymers recovered after the ESR signal disappeared. An electron source for the rereduction of the ZnTPP$^{•+}$ is probably water molecules. In the poly(A/Cd/ZnTPP) unimer micelle, the ZnTPP$^{•+}$ species are much better protected from the aqueous phase than those in poly(A/La/ZnTPP), leading to a much longer lifetime of the porphyrin cation radical in the former.

Neta *et al.*[19] reported that the half-life of the electrochemically generated cation radical of ZnTSPP was 6 s in aqueous solution. The half-life of ZnTPP$^{•+}$ in the poly(A/ZnTPP) system estimated in the present studies is close to the half-life of ZnTSPP$^{•+}$ reported in the literature.[19]

It is important to note here that the initial concentration and the lifetime of the porphyrin cation radical strongly depend on the type of the hydrophobic groups in the unimer micelles. Similar differences in the extent of the protection of chromophores in the hydrophobic microdomains of the La and Cd groups were recognized with compartmentalized pyrene and azobenzene moieties.[4−7] These differences were attributed to the difference in the local mobility of the La and Cd groups in the hydrophobic microdomains in the unimer micelles, the mobility of the Cd groups being much more restricted than that of the La groups, as indicated by spin−spin and spin−lattice relaxation times of ^{1}H-NMR.[4,7]

Conclusions

Electron transfer from the long-lived ^{3}ZnTPP* compartmentalized in the unimer micelles of poly(A/La/ZnTPP) and poly(A/Cd/ZnTPP) to PMPS, a self-destructive electron acceptor which is electrostatically concentrated on the surface of the unimer micelle, yields extremely long-lived ZnTPP$^{•+}$ within the hydrophobic microdomain in the unimer micelle. Since ZnTPP$^{•+}$ is separated from the bulk aqueous phase, subsequent reaction between the resulting ZnTPP$^{•+}$ and phenacyl radical from PMPS is prevented, leading to efficient accumulation of ZnTPP$^{•+}$ under steady-state irradiation with visible light. The ZnTPP$^{•+}$ species are much better protected in poly(A/Cd/ZnTPP) than in poly(A/La/ZnTPP); the porphyrin cation radical persisted for a much longer time in the former than in the latter. ZnTPP moieties in poly(A/ZnTPP), a reference copolymer, undergo CT interaction with PMPS in aqueous solution, leading to efficient quenching of ZnTPP fluorescence. In contrast, the ZnTPP moieties compartmentalized in the unimer micelles are prevented from the CT interaction and also from fluorescence quenching. However, the long-lived ^{3}ZnTPP* species in the unimer micelles undergo electron transfer to PMPS, despite the fact that the ZnTPP and PMPS species are separated inside and outside of the unimer micelle, respectively, and the electron transfer reaction is exothermic only by −0.04 eV.

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